Organic jan 12

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Effects in Organic Chemistry

① octet Condition
② Induction effect
③ Resonance / Mesomeric effect
④ Hyperconjugation
⑤ Aromaticity
→ Permanent

⑥ Electromeric effect ⇒ Temporary

① Octet effect

Complete octet > Incomplete octet

ⓐ $C = 1s^2\boxed{2s^2 2p^2} \rightarrow$ V.S.e = 4

[↿] [↿|↿|]

(i) $-\overset{|}{\underset{|}{C}}<$, $>C=$, $-C\equiv$, $=C=$

(ii) $\overset{\oplus}{C}$ ⇒ [↿] [↿|↿|] → vacant p

Carbocation

⊕
3σ (sp²)
Vacant p
Trigonal planar

$6e^-$ (octet incomplete)

(iii) $\overset{\ominus}{C}$ = [⇅] [↿|↿|↿]

Carbanion ⇓ octet Complete

[⇅|↿|↿|↿]
sp³ sp³ sp³ sp³

[⇅] [↿|↿|↿]

[⇅|↿|↿] [↿]
sp² sp² sp² p

$-\overset{\ominus}{\ddot{C}}=$ sp²

[⇅] [↿| |]

[⇅|↿] [↿|↿]
sp sp p p

⊖
2π
in sp hybrid orbital

Stability $\underset{sp}{\overset{\ominus}{C}\equiv} > \underset{sp^2}{-\bar{C}=} > \underset{sp^3}{\overset{\ominus}{C}}$

EN ∝ 1/s

(iv) $\dot{C}$ = [↿] [↿|↿|↿]

Carbon free Radical

[↿|↿|↿]
sp² sp² sp²

$7e^-$ (octet incomplete)

Exception

Note

$>C \frown\frown X \xrightarrow[\text{fission}]{\text{Homolytic}} \boxed{\dot{C}} + \dot{X}$

Carbon free Radical

$>C-X \xrightarrow[\text{fission}]{\text{heterolytic}} -\overset{\oplus}{C}< + X^{\ominus}$

$>C-X \xrightarrow{\text{''}} >C^{\ominus} + X^{\oplus}$

$\boxed{\overset{+}{C}, \overset{\circ}{C}, \overset{-}{C}} \rightarrow$ Carbon intermediates (Reactive in Nature)

ⓑ $N_7 = 1s^2 2s^2 2p^3$

[⇅] [↿|↿|↿]

i) $\ddot{N}$ (three single bonds) , $:N\equiv$, $-\ddot{N}=$

(ii) $\overset{\oplus}{N}$ ↳ 4 v.s.e like C $=\overset{+}{N}=$, $-\overset{+}{N}\equiv$, $-\overset{+}{N}=$, $-\overset{+}{N}<$

(iii) $N^{\ominus}$ ⇒ $-\overset{\ominus}{\ddot{N}}-$, $:\overset{\ominus}{N}=$

(iv) N^{-2} ⇒ $:\overset{2-}{\ddot{N}}-$

ⓒ Oxygen $O_8 = 1s^2\boxed{2s^2 2p^4}$

[⇅] [⇅|↿|↿]

$-\ddot{O}-$ $\ddot{O}=$

$-\overset{+}{\ddot{O}}-$ (three bonds) $:\overset{+}{O}\equiv$ $-\overset{+}{\ddot{O}}=$

$:\overset{\ominus}{\ddot{O}}-$

ⓓ Boron $B_5 = 1s^2\boxed{2s^2 2p^1}$

[↿] [↿|↿|] → Vacant p

octet incomplete

$\overset{\ominus}{B}$ = [↿] (2s) [↿|↿|↿] (2p)

↳ like C

$-\overset{\ominus}{B}<$, $-\overset{\ominus}{\underset{\|}{B}}-$, $-\overset{\ominus}{B}\equiv$, $=\overset{\ominus}{B}=$

octet complete

Stability $\overset{\ominus}{B} > B$

$\overset{+}{C} < \overset{\circ}{C} \lll \overset{\ominus}{C}$ → complete octet

octet incomplete

If octet condⁿ is same, then check charge

⇒ +ve on less EN atom is more stable

⇒ −ve on more EN " " " "

EN order

$\boxed{F > O > Cl \approx N > Br > I > S > C > P > H > \text{metals}}$

Stability $\overset{+}{S} > \overset{+}{N} > \overset{+}{O} \gg \overset{+}{C}$ → octet incomplete

octet complete

$\overset{\ominus}{C} < \overset{\ominus}{S} < \overset{\ominus}{N} < \overset{\ominus}{O}$

octet complete

Q1 Stability order

① $CH_3-\underset{\|}{C}(=O)-CH_3$ Ⓐ $CH_3-\boxed{\overset{+}{C}}-CH_3$ with O^- Ⓑ (octet incomplete) $CH_3-\overset{\ominus}{C}-CH_3$ with $\boxed{O^+}$ Ⓒ (octet incomplete)

octet incomplete $\boxed{\overset{+}{O} < \overset{+}{C}}$ Stability

$\boxed{A > B \gg C}$

② $CH_3-\overset{\oplus}{C}=O$ Ⓐ

$CH_3-C\equiv\overset{+}{O}:$ Ⓑ

$CH_3-CH=\overset{\oplus}{N}H_2$ Ⓒ

$\boxed{\overset{+}{N} > \overset{+}{O} > \overset{+}{C}}$

Stability → $\boxed{C > B > A}$

Ⅱ Inductive Effect (I-Effect)

↳ $\boxed{\text{Induction of Polarity}}$ in σ Bond due to ΔEN → electronegativity Difference

↳ In this effect σ Bonded e⁻ shifts towards more electronegative atom

↳ It is distance dependent effect.

$\boxed{\overset{\delta\delta\delta+}{C}-\overset{\delta\delta+}{C}-\overset{\delta+}{C}\rightarrow\overset{\delta+}{C}}\rightarrow\overset{\delta-}{Cl}$ → e⁻ withdrawing group (EWG) ↳ shows −I effect.

↳ σ e⁻ donating

Carbon Chain (+I effect)

+I effect showing Group (EDG) → e⁻ donating groups   [−ve species > neutral]

less EN, more loose e⁻

$\overset{\ominus}{C} > \overset{-}{N} > \overset{-}{O} > \overset{O}{\|}{C}-O^- > \underbrace{\overset{3^\circ}{C}R_3 > \overset{2^\circ}{C}HR_2 > \overset{1^\circ}{C}H_2-R > CH_3}$ > −D > −H

sp³

$-I$ effect order (EWG)

+ve > neutral

$\to NO_2$

$\to\to\overset{+}{N}R_3 > \to\overset{+}{S}R_2 > \to\overset{\oplus}{N}H_3 > \to\overset{\overset{sp^2}{\frown}}{\overset{\oplus}{N}}{\overset{\,O}{\underset{O^-}{\lessgtr}}} > -\overset{\overset{sp}{\frown}}{C}\equiv N > -CF_3 > -COOH >$

$-F > -CCl_3 > -Cl > -Br > -I > \boxed{-OCH_3 > -OH} > -O\underset{\text{Saturated}}{\textcircled{R}} > -NH_2 > -\underset{sp,\ \%s=50\%}{C\equiv C}- > -$⌬ or $-Ph$ $> -\underset{sp^2}{CH=CH}-$

I-Effect applications → Helps to compare stability of Carbon intermediates → $\dot{C}, C^+, \boxed{C^-}$ → EWG ↓es charge of C^- & ↑es the Stability

$\dot{C}, C^+$ → To stablise $\dot{C}, C^+$ → EDG provide e^- & ↑es stability

→ Helps to decide Acidic & Basic Strength orders

Q. Stability order:-

1) $\overset{\oplus}{C}H_2-CH_2-CH_2\leftarrow\boxed{O^-}$ $+I$

2) $\overset{\oplus}{C}H_2-CH_2-CH_2\to\textcircled{OH}$ $-I$

3) $\overset{\oplus}{C}H_2-CH_2-CH_2\to\textcircled{NH_2}$ $-I$

4) $\overset{\oplus}{C}H_2-CH_2-CH_2\leftarrow\underset{sp^3}{\textcircled{CH_3}}$ $+I$

$\boxed{1>4>3>2}$

$-I$ ($OH > NH_2$)

Q. Stability

(A)

$-I$

(B)

$-I$

(C)

$+I$

(D)

$-I$

$\boxed{D > B > A > C}$

$-I$ ($NO_2 > Cl > NH_2$)

Resonance & Mesomeric effect (M-effect)

(R-effect)

In this M-Effect :- πe^- $\boxed{\text{delocalisation}}$ occurs in Conjugated compounds & due to which we are able to write more than 1 Lewis Structure or structure for molecule or species.

- → These structures are called Resonating structures (R.S) or Canonical forms
- → R.S are Hypothetical or imaginary structures for any molecule.
- → No. of unpaired $\bar{e}$s must be same in all R.S for any molecule | species.
- → Properties of molecule | species are guided only by Resultant of all R.S called Resonance Hybrid (R.H) → Real form.
  - → All R.S may or may not be same.
  - → Most stable R.S, Contributes most to form R.H. → Have more Half life.

$\boxed{\text{Half life of Species} \propto \text{Stability}}$

- → Writing one R.S from other R.S, $\bar{e}$ delocalisation (movement) occurs & due to this molecule loses energy called Resonance Energy (R.E)

More stable is molecule, more will be its |R.E|.

- → RE is always released.
- → R.E is difference of Energy b/w most Stable R.S & R.H.

Atoms participating in R-effect or M-effect must be in Same plane so that their p-orbitals are parallel to each other for feasible π-Bond delocalisation

Q.

PE
R.S II
R.S III
R.S I
w
y
z
x
R.H

Let A comp has 3 R.S

R.S I

R.S II

R.S III

R·E will be 1) x ✓ 2) y 3) z 4) w

Atoms participating in R-effect or M-effect must be in same plane so that their p-orbitals are parallel to each other for feasible π-Bond delocalisation

In R-effect|M-effect, atoms never moves, only e⁻ density will move.

delocalised π Bonds or e⁻s have less energy Compared to localised e⁻s or π Bond (fixed)

Type of conjugation for delocalisatⁿ or Resonance

① $C=C-\overset{-}{C}\ |\ \overset{+}{C}\ |\ \overset{-}{O}\ |\ \ddot{O}\ |\ \overset{-}{N}\ |\ \ddot{N}\ |\ \ddot{S}\ |\ \overset{-}{S}\ |\ C=C\ |\ C\equiv C\ |\ C=O\ |\ N=O\ |\ S=O\ |\ C=N\ |\ C\equiv N\ |\ \dot{C}\ |$ Boron (B) $|\ \ddot{X}:$

eg $H_2C=CH-\overset{\ominus}{C}H_2$ R.S(I)
↕
$\overset{\ominus}{C}H_2-CH=CH_2$ R.S II } Identical

(R.H) $\overset{\delta-}{C}H_2\cdots CH\cdots \overset{\delta-}{C}H_2$ δ- → -1/2

(**) Bond length Carbons are partial double Bond

$CH_2=CH-CH=O$ R.S(I) more stable
↕
$\overset{\oplus}{C}H_2-CH=CH-O^-$ R.S(II) } Non-identical

R.H ⇒ $\overset{\delta+}{C}H_2\cdots CH\cdots CH\cdots \overset{\delta-}{O}$

Stability? eg Ⅰ $\overset{+}{C}H_2-OCH_3 \leftrightarrow CH_2=\overset{\oplus}{O}-CH_3$ +M or +R & -I } ⇒ +R > -I

Ⅱ $\overset{+}{C}H_2-\ddot{N}H_2 \leftrightarrow CH_2=\overset{\oplus}{N}H_2$ $N^+ > O^+$ stable; +R > -I

Ⅱ > Ⅰ

Note
Stability (follow the sequence)
① Complete octet > incomplete octet whether molecule is charged or uncharged.
② If octet condition is same, then neutral > charged Stable
③ In charged compounds Octet complete > incomplete octet
④ In charged, If condⁿ of octet is same, then -ve on more EN atom is more stable & +ve on less EN atom more stable.

②

$\overset{\ominus}{O}\ |\ \ddot{N}\ |\ \overset{\ominus}{C}\ |\ \overset{\ominus}{O}\ |\ \overset{-}{N}\ |\ \ddot{S}\ |\ \ddot{Cl}\ |\ \ddot{Br}\ |\ \ddot{I}:$

③

B – A ⇒ Atom having -ve charge or lone pair
A ⇒ Any atom
B ⇒ Boron

#
$\overset{+}{C}-C=O$ (repulsion, δ+)
$\overset{+}{C}-N=O$
$\overset{+}{C}-S=O$
$\overset{+}{C}-C=N$
$\overset{+}{C}-C\equiv N$
→ These C^+ are highly unstable So, no resonance

$\overset{+}{C}-C=C$

Q Stability order
①
octet incomplete
② $CH_3-\ddot{O}-BH_2$ +R>-I
③ $CH_3-NH-BH_2$ +R>-I
3>2>1

Q Stability order:

3>2>1

Identical R.S $CH_2=CH-\overset{\ominus}{C}H_2$
↕
$\overset{\ominus}{C}H_2-CH=CH_2$

$\overset{\delta-}{C}H_2\cdots CH\cdots \overset{\delta-}{C}H_2$ (δ-) → -1/2 (R.H)

Bond length b/w Carbon-Carbon is partial d.B

σ + l.p (localised) → No. of Hybrid orbitals

* During R-effect (M-effect), Hybridisatⁿ of atom does not change

delocalised
localised
2σ+1 Lp ⇒ sp²
dl
l
2σ+1 l.p(l) = sp²
$CH_2=CH-\ddot{O}H \leftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}-H$

delocalised
sp²
localised
sp²

(**)
localised
sp³
sp³
sp³

sp²
sp²
sp²
sp²
sp²
sp²

Stable
sp³
localised π Bond
sp³
sp³ (3σ+1 l.p)

Q

localised π
π-π Conj
A
π-π
π-π
extended Conj
B
C
this π-Bond is Cross-Conjugated or Cross-Reso.
Stability B>C>A

Q1 Which of the following species have R-effect|M-effect?

1)
π-π Conjugatⁿ
✓

2)
localised (no Resonance)
sp³
✗

3)
R.S II
π-π Conjugatⁿ
R.S I
sp³
sp³
CH₃ (+I effect)
R.S III

Stable
R.S(I) > R.S III > R.S(II)

4)
(π)(vacant p) Conjugatⁿ
p-vacant
more stable
✓

5)
π-(l.p) Conj
This oxygen is in Cross-Conjugatⁿ
✓
at a time only 3 atoms in Resonance

6)
l.p-π & π-π Conj
Extended Conjugatⁿ

Stability 6 > 5
Extended Reso causes more Stability. Comp 6 have more |R.E|

7)
is in Cross-Conjugatⁿ

8)
Extended Reso.

Stability 8 > 7

9)
δ+ = 1/2
⊕ is stabilised by Cross-Resonance

10)
Extended Conjugatⁿ
δ+ = 1/3
δ+
δ+
δ+

10 > 9 stable

11)
✗ N cannot form 5-Bonds

12)

✗

13)
Identical RS

doesn't show Resonance; only (-I)
-R or -M
& -I

14) $\overset{\ominus}{C}H_2-OCH_3$
no Resonance
-I effect OCH₃ Stabilises -ve of Carbon

$\overset{+}{C}-\ddot{O}$
$\overset{\ominus}{C}-\ddot{O}$

15)
R.S I
has vacant 3d
R.S II
R.S II > R.S I

Stable 17>18>16

16)
no Resonance
$\overset{\ominus}{C}$ is stabilised by -I effect of oxygen

17)
S stablises $\overset{-}{C}$ by Resonance (-R) & -I effect

18)

19) $CH_2=CH-\ddot{N}H_2$
L.p-π Conj
↕
$\overset{\ominus}{C}H_2-CH=\overset{\oplus}{N}H_2$

20) $CH_2=CH-\ddot{O}H$
L.p-π Conj
↕
$\overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}H$

$N^+ > O^+$ stable (19>20)

21)
3 Identical R.S

22)
2 Identical R.S

Stable 21 > 22

Comp having more Identical R.S is

23) $CH_2=CH-\overset{\oplus}{C}H-\ddot{O}CH_3$
π-(+ve)
(l.p)(+ve) Conj

24) $CH_2=CH-\overset{\oplus}{C}H\rightarrow CH_2\rightarrow \ddot{O}CH_3$
sp³
-I only

Cnj

$\boxed{\text{Stability } 23>24}$

no +R or +M

more Stable than
Comp. having less identical
R.S

+M or +R and
-I effect
But +R > -I

Note: ① If any atom have more than 1 l.p, then at a time only one lone pair is delocalised (ie; participate in resonance).

② If any atom have $\boxed{\text{l.p}}$ as well as $\boxed{\pi \text{ Bond}}$ then l.p is localised (does not participate in Resonance)

③ Groups which donate ēs via R.effect or M.effect have +R or +M effect.

④ " " accept ēs via " " " " -R or -M effect.

Q. Stability order

+I, +R

1)

2)

3)

$\boxed{1<2<3}$

Attacking species

$\boxed{Nu^{\ominus}}$
Nucleophile
⇓
ē Rich
or
ē donor
→ All Lewis Base

$\boxed{E^{+}}$
Electrophile
⇓
ē seeking species
or
ē deficient species
→ All Lewis Acids

more ē density in Ring

Q. Which Benzene Ring is most Activated (Reactive) towards $E^{\oplus}$ (Electrophile)?

1)

2)

3)

4)

$\boxed{1>4>3>2}$

-I (OH > NH_2)

(*) $\boxed{NH_2 \text{ is Better Donor}}$

#

O⊖ | N̄ | ÖH | ÖR | N̈H2 | N̈R2 | N̈HR | O-C(=O)-R | -NH-C(=O)-R | X

$\boxed{+R}$ showing Group

#

C(=O)-R | -C(=O)-H | C(=O)OH | C(=O)NH2 | -C(=O)-O-C(=O)-R | -C≡N | -NO2

-R showing Groups